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(19) (CA) **CANADIAN PATENT** (12)

(54) (Meth)Acrylate Esters

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Abstract of the disclosure:

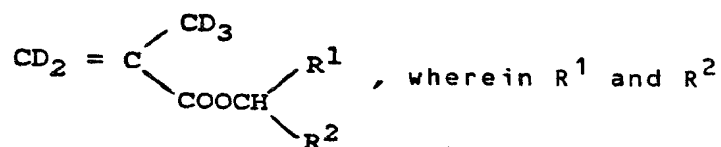
Esterification of wholly or partially deuterated (meth)-acrylic acid with alcohols, which have only a little hydrogen or none at all in the molecule, gives monomers which, after polymerization, give transparent polymeric materials with low attenuation of light waves and with a high glass temperature.

Description:

(Meth)acrylate esters

The invention relates to esters of wholly or partially deuterated (meth)acrylic acid with alcohols, which have only a little hydrogen or none at all in the molecule, to processes for the preparation of these esters and to their use for the preparation of transparent polymeric materials for optical fibers. Various esters of perdeuterated methacrylic acid and their use for the preparation of transparent polymers for optical fibers are known.

Thus, fluoroalkyl esters of deuterated methacrylic acid of the formula



are lower fluoroalkyl radicals or hydrogen atoms, but at least one of the two radicals is required to be a lower fluoroalkyl radical, are known (cf. Japanese Published Application 61-20,906). 2,2,2-Trifluoroethyl, 2,2,3,3-tetrafluoro-1-propyl and 1,1,1,3,3,3-hexafluoro-2-propyl are mentioned by name. On the other hand, these esters still contain a relatively large number of hydrogen atoms in the molecule, which have an attenuating effect on the light transmission of the polymers prepared from these esters.

Esters of wholly or partially deuterated methacrylic acid with borneol, isoborneol and fenchyl alcohol are also known (cf. EP-A 144,712; US Patent 4,575,188). However, the methyl groups in the alcohol components of these esters make a considerable contribution to the residual hydrogen

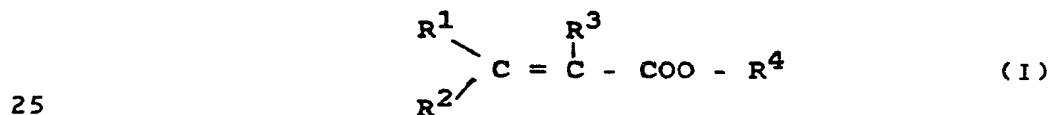


content of the esters, since their hydrogen atoms are difficult to replace by deuterium.

As is known, one hydrogen atom per mole of monomer increases the attenuation of the light transmission of the polymer in the wavelength region from 600 to 800 nm due to absorption by about 11 dB/km. It was then desirable to find monomers which provide the polymeric transparent materials prepared from them by polymerization with the lowest possible attenuation. At the same time, the transparent polymeric materials should have a glass point T_G which is higher than that of the hitherto mainly used polymethyl methacrylate ($T_G = 105^\circ\text{C}$).

It has been found that the object can be achieved when wholly or partially deuterated (meth)acrylic acid is esterified with certain alcohols which contain only a little hydrogen or none at all in the molecule.

Thus, the invention relates to a compound of the formula (I)



wherein

R^1 and R^2 are identical or different and are a hydrogen atom or deuterium atom,

R^3 is H, D, $-\text{CH}_3$, $-\text{CH}_2\text{D}$, $-\text{CHD}_2$ or $-\text{CD}_3$ and

R^4 is one of the groups $-\text{C}(\text{CH}_3)_2-\text{CN}$, $-\text{C}(\text{CD}_3)_2-\text{CN}$,



(bicyclo-2.2.1-hept-2-yl) or



(tricyclo-2.2.1^{2,6}-hept-3-yl),

it being possible for the rings to be deuterated, and, if R^3 is $-CD_3$, R^4 can also be $-C(CF_3)_2-CF(CF_3)_2$, $-CF(CF_3)_2$ or $-CD(CF_3)_2$.

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The invention also relates to a process for their preparation and to their use for the preparation of transparent polymeric materials.

10 In the formula (I), R^1 and R^2 are preferably a deuterium atom, R^3 is preferably a deuterium atom or one of the groups $-CH_3$, $-CH_2D$, $-CHD_2$ or $-CD_3$, especially a deuterium atom or a perdeuteromethyl group, and R^4 is preferably

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(bicyclo-2.2.1-hept-2-yl, norbornyl) or



(tricyclo-2.2.1.0²⁻⁶-hept-3-yl),

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it being possible for the rings to be deuterated, and in the case of $R^3 = -CD_3$ can also be

$-C(CF_3)_2-CF(CF_3)_2$, $-CF(CF_3)_2$ or $-CD(CF_3)_2$.

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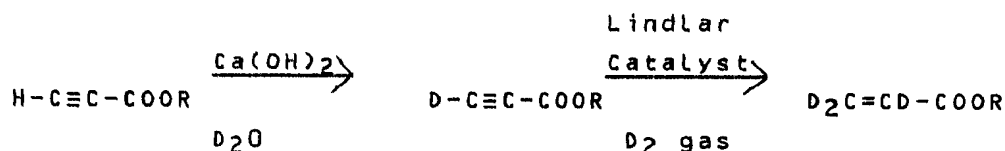
The acid components of the esters according to the invention are thus preferably deuterated acrylic acid and methacrylic acid. The preparation of the deuterated acids is known per se, and it can be carried out, for example, in

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Methyl (meth)acrylate, deuterium oxide, a noble metal salt and a polymerization inhibitor are stirred for several hours at a temperature of around 100°C in a reactor.

35

It is also possible to obtain perdeuterated acrylic acid in accordance with the following reaction equation:



If required, the corresponding acids can be obtained from the esters.

For the further conversion (esterification), the acid of the formula II



wherein R^1 , R^2 and R^3 are as defined above, is used as such ($\text{R}^5 = \text{OH}$ or OD) or in the form of an acid halide ($\text{R}^5 = \text{Cl}$ or Br , preferably Cl). The acid halide is prepared by means of a conventional halogenating agent, for example oxalyl chloride, phosphorus pentachloride, phosphorus trichloride, phosphorus oxychloride, benzoyl chloride, benzotrichloride, phosphorus tribromide and especially thionyl chloride. The halogenation with thionyl chloride is preferably carried out in the presence of a catalyst such as dimethylformamide. The reaction is carried out in an aromatic hydrocarbon, for example toluene, xylene or trimethylbenzene, as the solvent and the reaction temperature is in the range from 50 to 100°C, preferably 70 to 90°C.

The (meth)acrylic acid or the acid halide is then reacted with a compound of the formula (III)



wherein R^4 is as defined above.

The acid halide is preferably used for the esterification of the alcohols $\text{HO-C(CH}_3\text{)-CN}$, $\text{HO-CD(CF}_3\text{)}_2$, $\text{HO-CF(CF}_3\text{)}_2$

and $\text{HO}-\text{C}(\text{CF}_3)_2-\text{CF}(\text{CF}_3)_2$.

The esterification is preferably carried out in a solvent, and the reaction temperature is -10 to 50°C , preferably 0 to 25°C . The solvent used is a polar organic solvent, especially a symmetrical, asymmetrical or cyclic ether, for example diethyl ether, dipropyl ether, diisopropyl ether, tert.-butyl methyl ether, tetrahydrofuran and dioxane, an aliphatic halogenohydrocarbon, preferably chlorohydrocarbon, for example dichloromethane, trichloromethane, tetrachloromethane, 1,1-dichloroethane and 1,2-dichloroethane, an aromatic halogenohydrocarbon, preferably chlorohydrocarbon, for example chlorobenzene and 1,2- or 1,3-dichlorobenzene, or an aliphatic or aromatic nitrile, for example acetonitrile and benzonitrile. The solvent can also be a mixture of several polar solvents. It is expedient to carry out the esterification of the acid halide with the alcohol in the presence of an organic base, especially a trialkylamine having 1 to 4 carbon atoms in each of the alkyl groups. The base is employed in a quantity from 0.5 to 2 mole, preferably 0.8 to 1.2 mole (relative to 1 mole of acid halide). The ester obtained is isolated from the reaction mixture by distillation, preferably under a pressure of 1,013 to 200 mbar, or - after removal of the solvent by distillation - by hot extraction of the solid residue with a non-polar solvent, preferably an aliphatic hydrocarbon such as n-hexane, and subsequent crystallization. It is appropriate to carry out the distillation in the presence of a conventional polymerization inhibitor, for example hydroquinone or hydroquinone monomethyl ether; the latter is used in a quantity from 100 to 500 ppm (relative to acid halide). The bottom temperature is in the range from 20 to 100°C , preferably 30 to 85°C . For further purification, the ester is distilled again, preferably under a reduced pressure, or recrystallized.

The alcohol is employed in a quantity of 0.5 mole, preferably 0.8 to 1.2 mole (relative to 1 mole of (meth)acrylic acid).

Operation in the presence of a dehydrating agent, for example oleum, represents a further esterification method.

5 The (meth)acrylic acid esters of bicycloheptyl (norbornyl) and tricycloheptyl alcohol can be prepared according to known methods by acid-catalysed addition of (meth)acrylic acid to bicycloheptene or bicycloheptadiene respectively.

10 After known free-radical polymerization by themselves, with one another and/or with other comonomers, for example methacrylic acid esters of aliphatic or alicyclic alcohols, the esters according to the invention give transparent polymeric materials which show low attenuation of incident light and a high glass temperature T_g . The alcohols used
15 for the preparation of the esters according to the invention contain either no hydrogen or only a little hydrogen in the molecule.

20 Compared with borneol and isoborneol, the methacrylates of which are known, the cyclic alcohols of the norbornene type (bicyclo-2.2.1-heptan-2-ol and tricyclo-2.2.1.0²⁻⁶-heptan-3-ol) have the advantage of a more favorable C/H ratio and offer the possibility of replacing all the hydrogen atoms by deuterium by means of catalytic H/D exchange with
25 D₂O, on the basis of a Wagner-Meerwein rearrangement. Since a mixture of exo- and endo-norborn-2-yl alcohol or exo- and endo-tricyclohept-3-yl alcohol is formed in the addition reaction, the anisotropy of a polymer produced from the esters is reduced, whereby the transparence is
30 increased.

The transparent polymeric materials obtained from the esters are used for the production of optical fibers, resist material, lenses, optical data storage media and
35 other transparent articles.

The invention is explained in more detail by the examples which follow.

Example 1

2-Cyano-isopropyl methacrylate

- 5 9 ml of 2-cyano-isopropyl alcohol (0.098 M) were added to
10 ml of methacrylic acid chloride (0.103 M) in 50 ml of
methyl tert.-butyl ether, 15 ml of triethylamine were then
added dropwise with ice-cooling and the mixture was stirred
for 1 hour. The triethylammonium hydrochloride was filtered
10 off, and the filtrate was freed of solvent and distilled in
vacuo. 7.9 g of 2-cyano-isopropyl methacrylate were dis-
tilled off at 49 - 50°C/1.3 mbar, corresponding to 51.6%
yield.
IR(CH₂Cl₂): C=O at 1750 cm⁻¹, C≡N at 2290 cm⁻¹ (weak)
15 Molecular mass: 153

Example 2

- The perdeuterated compound was prepared analogously from
20 methacrylic acid chloride-D₅ and 2-cyano-isopropyl alcohol-
D₆. Yield 90 g, boiling point 53°C/1.3 mbar.
Molecular mass: 164

Example 3

- 25 50 mg of di-lauroyl peroxide were in each case dissolved
in 5 ml of the 2-cyano-isopropyl methacrylate according
to each of Examples 1 and 2, and the solutions were kept
for 20 hours at 50°C and then for 2 hours at 90°C. This
30 gave glass-clear polymers of glass temperature 117°C and
a decomposition temperature 220°C.

Example 4

- 35 Norbornyl methacrylate

165 g of norbornene (= 1.75 M) were dissolved in 100 ml of
methylene chloride, and 1 g of tert.-butylpyrocatechol was
added as a stabilizer. With stirring and cooling, a

mixture of 150 ml of methacrylic acid and 15 ml of BF_3 etherate was added dropwise at $30 - 40^\circ\text{C}$ in the course of 2 hours.

The mixture was stirred for a further 2 hours, and the solution was washed with water until neutral, dried and

5 concentrated by distillation. The viscous residue was distilled in an oil pump vacuum at boiling point $=52^\circ\text{C}/0.013$ mbar. This gave 210 g of norbornyl methacrylate, corresponding to 66% yield. $\text{IR}(\text{CH}_2\text{Cl}_2)$ $\text{C}=\text{O}$ at 1710 cm^{-1} .
Molecular mass: 180

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The H^1 -NMR spectrum was consistent with the indicated structure.

Example 5

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Starting from methacrylic acid- D_5 and partially deuterated norbornene, it was possible to prepare the deuterated ester (partially deuterated in the norbornyl radical) analogously to Example 4, the yield and boiling point corresponding to

20 the undeuterated compound.

Example 6

5 ml of each of the pure compounds from Example 4 and

25 Example 5 were kept with 50 mg of dilauroyl peroxide in each case for 20 hours at 50°C and then for 2 hours at 90°C . This gave glass-clear, hard polymers. The differential thermal analysis gave 2 T_g values of 120.8°C and 172°C , decomposition temperature 225°C .

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Example 7

Perfluoro-dimethylbutyl perdeutero-methacrylate

35 40 g of perfluorodimethyl-butan-2-ol were added to 10 ml of methacrylic acid chloride- D_5 , dissolved in 50 ml of methyl tert.-butyl ether. 17 ml of triethylamine were added dropwise with stirring and cooling. The temperature was maintained at 20°C . After 1 hour, the precipitated triethyl-

ammonium hydrochloride was filtered off with suction and the filtrate was distilled. The perfluorodimethylbutyl perdeuteromethacrylate boiled at 45°C/11 mbar. The yield was 14 g, corresponding to 28.5% of theory.

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The ester was polymerizable with 1% of dilauroyl peroxide (20 hours at 50°C, 1 hour at 90°C) and gave a glass-clear polymer having a glass temperature of 111°C.

10 Example 8

Tricyclo-2.2.1.0^{2.6}-hept-3-yl acrylate

30 ml of norbornadiene (= 0.32 M) were dissolved in 50 ml of CH₂Cl₂, and a mixture of 20 ml of acrylic acid (= 0.29 M), 0.5 g of tert.-butylpyrocatechol and 3 ml of BF₃ etherate were added dropwise to the solution at 20°C with stirring.

A slightly exothermic reaction was observed. After 6 hours, the batch was transferred into a separating funnel and washed therein with water, and then dried. In the distillation which followed, 12.6 g of a substance passed over at 60°C and 1.7 mbar. The substance had a molar mass of 164, and the H¹- and C¹³-NMR spectrum showed the structure of a tricyclo-2.2.1.0^{2.6}-hept-3-yl acrylate. Yield 26.5%.

Example 9

Tricyclo-2.2.1.0^{2.6}-hept-3-yl methacrylate

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Analogously to Example 8, a mixture of 25 ml of methacrylic acid, 5 ml of BF₃ etherate and 1 g of tert.-butylpyrocatechol (as stabilizer) was added to 35 ml of norbornadiene dissolved in 50 ml of CH₂Cl₂. After 6 hours of a slightly exothermic reaction, the batch was worked up as in Example 8.

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Boiling point 75° - 85°C at 1.7 mbar, yield 32 g = 62% of theory: molecular mass 178.

The H^1 - and C^{13} -NMR spectrum showed the structure of a tricyclo-2.2.1.0^{2,6}-hept-3-yl methacrylate.

Example 10

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Deuterohexafluoroisopropyl perdeutero-methacrylate

30 ml of perdeuterated methacrylic acid and 45 ml of perdeuterated hexafluoroisopropanol (prepared by catalytic
10 hydrogenation of hexafluoroacetone with D_2 on a Pd/C catalyst) were mixed with 75 ml of 16% oleum. During the reaction, the temperature rose to 40°C. After 15 minutes, the mixture was transferred into a thin-layer evaporator and distilled at a wall temperature of 130°C under a vacuum
15 of 44 mbar. At a top temperature of 50 to 60°C, 60 g of crude deuterohexafluoroisopropyl perdeuteromethacrylate passed over, and this was distilled once more. This gave 50 g of end product, corresponding to a yield of 60% of theory.

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The ester was polymerizable by means of 0.1% by weight of dilauroyl peroxide and gave a polymer having a T_g value of 74°C and a decomposition temperature higher than 200°C.

25 Example 11

Perfluoroisopropyl perdeutero-methacrylate

12.9 g (0.222 M) of potassium fluoride were suspended in
30 80 ml of diglycol dimethyl ether. 33 g (0.198 M) of hexafluoroacetone were passed into this suspension at room temperature. The batch was then stirred for a further 2 hours and the undissolved potassium fluoride was then separated off. 22 g (0.2 M) of methacrylic acid chloride- D_5
35 were added dropwise to the filtrate at room temperature and the reaction mixture was stirred for a further hour. After the solid formed had been separated off, the filtrate was distilled.

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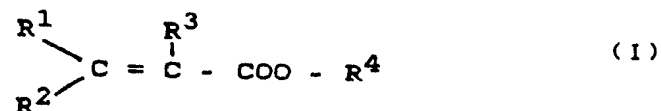
Colorless liquid, boiling point 45.2 - 45.4 °C/80 mbar.

Yield 32 g = 64% of theory.

5 The ester was polymerizable by means of 0.5% by weight of dilauroyl peroxide for 24 hours at 50°C, to give a glass-clear polymer having a T_g value of 76°C.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A compound of the formula (I)



wherein

R^1 and R^2 are identical or different and are a hydrogen atom or deuterium atom,

R^3 is H, D, $-\text{CH}_3$, $-\text{CH}_2\text{D}$, $-\text{CHD}_2$ or $-\text{CD}_3$ and

R^4 is one of the groups $-\text{C}(\text{CH}_3)_2-\text{CN}$, $-\text{C}(\text{CD}_3)_2-\text{CN}$,



(bicyclo-2.2.1-hept-2-yl) or



(tricyclo-2.2.1.0^{2.6}-hept-3-yl),

wherein the rings may be deuterated, and wherein at

least one of R^1 to R^4 contains a deuterium atom, and,

if R^3 is $-\text{CD}_3$,

R^4 can also be $-\text{C}(\text{CF}_3)_2-\text{CF}(\text{CF}_3)_2$, $-\text{CF}(\text{CF}_3)_2$ or $-\text{CD}(\text{CF}_3)_2$.

2. A compound as claimed in claim 1, wherein, in the formula (I),

R^3 is $-\text{D}$, $-\text{CH}_3$, $-\text{CH}_2\text{D}$, $-\text{CHD}_2$ or $-\text{CD}_3$ and

R^4 is



(bicyclo-2.2.1-hept-2-yl)



(tricyclo-2.2.1.0^{2.6}-hept-3-yl),

wherein the rings may be deuterated, and, in

the case of $\text{R}^3 = -\text{CD}_3$, can also be $-\text{C}(\text{CF}_3)_2-\text{CF}(\text{CF}_3)_2$, $-\text{CF}(\text{CF}_3)_2$ or $-\text{CD}(\text{CF}_3)_2$.

3. A process for preparing the compound as defined in claim 1 by reacting a compound of the formula (II)



wherein R^1 , R^2 and R^3 are as defined in claim 1 and R^5 is a halogen atom, an OH group or an OD group, with a compound of the formula (III)

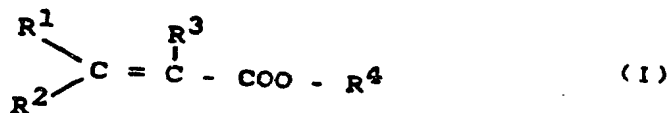


wherein R^4 is as defined in claim 1, at a temperature from -10 to 50°C in the presence of a catalyst.

4. The use of compound of the formula (I) as claimed in claim 1 for the production of transparent polymeric materials.

5. The compound of the formula (I) as claimed in claim 1 for use in the production of transparent polymeric materials.

6. The use of a compound of the formula (I)



wherein

R^1 and R^2 are identical or different and are a hydrogen atom or deuterium atom,

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R^3 is D, $-\text{CH}_2\text{D}$, $-\text{CHD}_2$ or $-\text{CD}_3$ and

R^4 is one of the groups $-\text{C}(\text{CH}_3)_2-\text{CN}$, $-\text{C}(\text{CD}_3)_2-\text{CN}$,



(bicyclo-2.2.1-hept-2-yl) or



(tricyclo-2.2.1²-6-hept-3-yl),

wherein the rings may be deuterated, and,

if R^3 is $-\text{CD}_3$,

R^4 can also be $-\text{C}(\text{CF}_3)_2-\text{CF}(\text{CF}_3)_2$, $-\text{CF}(\text{CF}_3)_2$ or $-\text{CD}(\text{CF}_3)_2$,
for the production of polymeric materials which show
low attenuation of incident light and a high glass
temperature (T_g).



SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente